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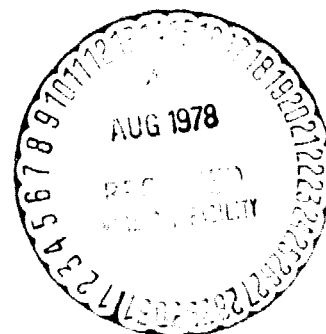
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**AN IMPROVED METHOD FOR ANALYSIS OF
HYDROXIDE AND CARBONATE IN ALKALINE
ELECTROLYTES CONTAINING ZINC**

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AN IMPROVED METHOD FOR ANALYSIS OF HYDROXIDE AND CARBONATE
IN ALKALINE ELECTROLYTES CONTAINING ZINC

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ABSTRACT

A simplified method for titration of carbonate and hydroxide in alkaline battery electrolyte is presented involving a saturated KSCN solution as a complexing agent for zinc. Both hydroxide and carbonate can be determined in one titration, and the complexing reagent is readily prepared. Since the pH at the end point is shifted from 8.3 to 7.9 - 8.0, m-cresol purple or phenol red are used as indicators rather than phenolphthalein. Bromocresol green is recommended for determination of the second end point of a pH of 4.3 to 4.4.

INTRODUCTION

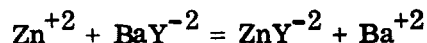
Silver-zinc batteries are being used for terrestrial and space applications, and nickel-zinc batteries are under serious consideration for electric vehicle propulsion and other terrestrial applications. Greater economy and usage of these batteries would result if the battery life were extended. Systematic improvement is possible if the modes of failure are known and understood; this often requires a determination of the hydroxide and carbonate content of the electrolyte as well as that of the zinc. The hydroxide and carbonate content of an alkaline sample are usually determined by titration with a standard acid. Two end points are used. One is at a pH ~8.3 and the other at a pH ~4.3. In one method excess Ba^{+2} is added since $\text{Ba}(\text{OH})_2$ is soluble at pH 8 and BaCO_3

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is insoluble. Thus only OH^- is neutralized at the first end point, and only CO_3^{-2} is neutralized between the two end points. If no Ba^{+2} is present, the CO_3^{-2} is converted to HCO_3^- at the first end point. The HCO_3^- is neutralized to carbonic acid between the two end points. The details can be found in most college textbooks of analytical chemistry.

In the titration of battery electrolyte the presence of dissolved zinc species from the zinc electrode introduces errors at the first end point due to the formation of zinc hydroxides and carbonates, both of which are insoluble at $\text{pH} \sim 8$. A previous method developed at NASA Lewis Research Center (ref. 1) utilized the barium salt of EDTA (ethylenediaminetetraacetic acid) in an excess of BaCl_2 to complex the zinc ions by the reaction



where Y^{-4} is the anion of ethylenediaminetetraacetic acid. In the titration to $\text{pH} \sim 8$, all of the hydroxide will be neutralized and none of the carbonate. A separate sample is taken for determination of total alkalinity by titration to $\text{pH} \sim 4.3$. Since both $\text{Zn}(\text{OH})_2$ and ZnCO_3 are soluble at this pH, there is no interference by the zinc at the second end point.

This procedure has the advantage of determining OH^- without any interference from the zinc species. However, a second sample without the BaEDTA reagent must be titrated to determine the CO_3^{-2} content because EDTA is a weak acid. This means that the reagent would also significantly affect the amount of standard acid used in a titration if its initial pH were different from that of the end point. In addition, the BaEDTA solution must be adjusted to a pH of 8 just before the titration since a precipitate, presumably BaEDTA, forms within a few hours of this pH. For further details, the reader is referred to the original publication. For these reasons, a second method has been developed which utilizes KSCN as the complexing reagent instead of EDTA.

Thiocyanate was investigated as a complexing agent for Zn^{+2} because thiocyanic acid is a strong acid and the presence of its salts would not affect the titration to either end point significantly.

THEORY

The interference due to Zn^{+2} can be avoided by the use of SCN^- if the complex does not permit the precipitation of ZnCO_3 or Zn(OH)_2 at pH ~ 8 . The possibility can be investigated by using the constants for the various reactions which are involved. Table I lists the pertinent ones.

TABLE I. - EQUILIBRIUM CONSTANTS FOR PERTINENT REACTIONS
IN THE TITRATION OF ALKALINE BATTERY
ELECTROLYTES CONTAINING ZINC

Reaction	Constant	Reference
$\text{ZnCO}_3 = \text{Zn}^{+2} + \text{CO}_3^{-2}$	2×10^{-10}	2
$\text{Zn(OH)}_2 = \text{Zn}^{+2} + 2 \text{OH}^-$	4.7×10^{-17}	2
$\text{Zn(OH)}_4^{-2} = \text{Zn}^{+2} + 4 \text{OH}^-$	2.8×10^{15}	2
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{-2}$	5.6×10^{-11}	3
$\text{Zn}^{+2} + \text{SCN}^- = \text{ZnSCN}^+$	$\sim 2.4 \times 10^{-4}$	4

The SCN^- complex is rather weak. However, the solubility of KSCN is large enough (~ 10 M) so that enough can be added to prevent the precipitation of ZnCO_3 and possibly Zn(OH)_2 at the first end point although both may precipitate in the intermediate stages.

We will assume for purposes of calculation that the initial battery electrolyte has the following approximate concentrations: $[\text{OH}^-] = 10$ M, $[\text{CO}_3^{-2}] = 1$ M, and $[\text{Zn}^{+2}] = 1$ M. These are typical concentrations for actual electrolytes. If a 0.5 cm^3 sample is taken for analysis, diluted, and aliquots amounting to $1/5$ of this solution analyzed, the amounts of OH^- , CO_3^{-2} , and Zn^{+2} in each sample will be 1 mmole (millimole), 0.1 mmole, and 0.1 mmole,

respectively. If the sample is diluted to a final volume of 100 cm^3 , the respective concentrations of these ions will be 10^{-2} , 10^{-3} , and 10^{-3} M .

If the concentration of SCN^- in the solution at the start of the titration is 5 M , since

$$\frac{[\text{Zn}^{+2}][\text{SCN}^-]}{[\text{ZnSCN}^+]} = 2.4 \times 10^{-2}$$

then

$$\frac{[\text{Zn}^{+2}]}{[\text{ZnSCN}^+]} \sim 5 \times 10^{-3}$$

i.e., almost all of the zinc will be complexed with the SCN^- . The concentration of the uncomplexed zinc will be about $5 \times 10^{-6} \text{ M}$, and the concentration of hydroxide will be 10^{-6} M at the end point. Therefore, the ion products for $\text{Zn}(\text{OH})_2$ and ZnCO_3 will be $\sim 5 \times 10^{-18}$ and 2.8×10^{-11} , less than the solubility product constants, and both will be soluble. If the zinc concentration had not been reduced below 10^{-3} M by complexing with the thiocyanate, both would be insoluble at this point.

Using the above constants, one finds that in the initial battery electrolyte, zinc is soluble due to the formation of the tetrahydroxyzincate ion, but that $\text{Zn}(\text{OH})_2$ precipitates when the sample is diluted before taking of aliquots if the OH^- concentration falls below about 1 M . However, $\text{Zn}(\text{OH})_2$ forms supersaturated solutions readily, especially in the presence of saturated KSCN , so that if the aliquots are taken within about an hour, no precipitation usually occurs. Zinc carbonate will also precipitate in the intermediate stages even in the presence of KSCN , but as shown above, both precipitates will dissolve just before the end point is reached.

EXPERIMENTAL

Materials and Apparatus

All reagents were C.P. chemicals. Na_2CO_3 was prepared by heating NaHCO_3 to 270° to 300°C for several hours. The zinc stock solution was prepared from $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ and standardized by titration with EDTA.

Titration curves were made using an automatic potentiometric titrator having a derivative mode as well as a pH mode. In addition, the rate of delivery of titrant is automatically adapted to the slope of the titration curve, and the rate of adaptation can be varied.

The indicators used are described below.

Indicator	Range	Color	
		Acid	Base
Phenolphthalein	8.2 to 10.0	Colorless	Pink
m-cresol purple	7.4 to 9.0	Yellow	Purple
Phenol red	6.8 to 8.4	Yellow	Red
Methyl orange	3.1 to 4.4	Red	Orange-yellow
Bromcresol green	3.0 to 4.6	Yellow	Blue

Titration Curves

In order to check the experimental method for precision and accuracy, solutions were prepared to simulate typical compositions obtained when samples of battery electrolyte were diluted for titration. Figure 1 shows a titration curve for a solution containing 0.859 ± 0.003 mmoles (millimoles) KOH, 0.012 mmoles of K_2CO_3 (as impurity in the KOH), 0.5150 ± 0.0010 mmoles of Na_2CO_3 , and 0.1274 ± 0.001 mmoles of ZnSO_4 with and without the addition of 28 ml of saturated KSCN, which is the equivalent amount added if the battery electrolyte is diluted as described below. Curve A is the titration curve without the addition of KSCN. The inflection points are not sharp and do not

occur at the stoichiometric end points. In curve B, saturated KSCN has been added to the same solution. This shows satisfactory inflections at the proper equivalence points. Curve C is the derivative curve for the same solution as curve B. A small amount of acid, 0.021 mmoles in this case, is consumed in titrating the KSCN to the second end point and for precision a blank correction should be made. The calculated mmoles of HCl to the first and second end points are 1.386 ± 0.003 and 1.934 ± 0.003 including the KSCN correction. For five determinations we find 1.386 ± 0.004 and 1.937 ± 0.006 mmoles.

In figure 2 similar titration curves are given for lower levels of carbonate and zinc. The calculated values to the first and second end points are 1.094 ± 0.004 and 1.341 ± 0.004 mmoles, and the experimental values 1.099 ± 0.003 and 1.349 ± 0.004 . In figure 3 a curve is shown for a low level of carbonate showing the utility of the derivative curve. The first end point is much more readily obtained when the derivative is plotted rather than the pH when low levels of carbonate are present.

The reason for the necessity of a blank correction for titration of KSCN to the second end point is not clear. Several authors have found no evidence for association of SCN^- with H^+ , but one author has found a slight degree of association (ref. 5). Small amounts of impurities in the highly concentrated solutions used could account for the blank. It is advisable to determine the blank correction with a sample of the actual KSCN solution to be used in the analyses.

Determination of the End Points by pH Meter or Indicators

If an automatic titrator is not available, a pH meter or indicators can be used to determine the end point. In the standard method for determination of hydroxide and carbonate, phenolphthalein is used to detect the first end point (pH ~ 8.3) by titration to a very pale pink color. Methyl orange or bromocresol green are used to determine the second end point at a pH of

around 4.3. In the method described here, the pH at the first end point is shifted from 8.3 to 7.9 - 8.0. The reason for this is not known, but possibly is due to the effects of the high concentration of KSCN (about 5 M in the final solution) on the activity coefficients of the ions present. If the end point is determined by a pH meter, the titration to the first end point should be carried out to a pH of about 7.9 to 8.0. If indicators are to be used, phenolphthalein is no longer satisfactory since it changes from pink to colorless before the end point is reached. Phenol red or m-cresol purple have been found satisfactory. In both cases, titration is carried out to the appearance of a faint yellow color in the solution. Metacresol purple is preferable due to a more distinctive color change. For determination of the second end point, either methyl orange or bromcresol green can be added after the first end point is reached. Due to the presence of the yellow form of m-cresol purple or phenol red in the solution, the color at the end point will be somewhat different from the color of these indicators alone. If methyl orange is used, the second end point is reached when the solution becomes a peach color, and if bromcresol green is used, the end point is reached when the solution becomes completely yellow with no tinge of green. Bromcresol green is preferable, again since it has a more distinctive color change. If a pH meter is used, titration to a pH of about 4.3 is satisfactory.

Recommended Analytical Procedure

A 0.5 cm^3 sample of electrolyte is withdrawn from the battery with a syringe or pipet and placed in a 25 cm^3 volumetric flask. Fifteen cm^3 of saturated KSCN are added and the solution diluted to the mark with distilled water. The solution is immediately shaken and 5 cm^3 aliquots withdrawn. Zinc hydroxide will precipitate at this pH, but ordinarily no precipitate forms for at least a half-hour since the hydroxide readily forms supersaturated solutions. The addition of the saturated KSCN seems to help retard the onset

of precipitation. If a precipitate does form, it does not settle for some time so that accurate aliquots can still be taken.

Since the battery electrolyte is quite viscous, there is a question as to the accuracy of sampling with a syringe or pipet. Experiments in our laboratories indicate $\pm 2\%$ accuracy using a syringe, $\pm 1\%$ with pipets; this is sufficient for most purposes. Greater accuracy can be obtained by weighing samples into a 10 cm^3 volumetric flask before dilution with KSCN. In this case, 2 cm^3 aliquots would be taken.

Twenty-five cm^3 of saturated KSCN are added to each aliquot and the solution is titrated with standardized HCl of about 0.05 M concentration. If an automatic titrator is available, it can be used in either a pH or derivative mode. The latter is especially useful when there are very small quantities of carbonate in the solution, as shown in figure 3. In the absence of an automatic titrator, a pH meter can be used to titrate to pH values of 7.9 to 8.0 for the first end point and 4.3 to 4.4 for the second end point. Alternatively, either m-cresol purple or phenol red can be used to determine the first end point and either bromcresol green or methyl orange to determine the second.

CALCULATIONS

This titration gives the CO_3^{-2} content of the electrolyte as well as the amount of OH^- from both the KOH and the $\text{Zn}(\text{OH})_4^{-2}$ in the solution. Zinc oxide will dissolve in KOH by the reaction $\text{ZnO} + \text{H}_2\text{O} + 2\text{KOH} = \text{Zn}(\text{OH})_4^{-2}$. At the first end point, the zinc will be complexed as ZnSCN^+ so that each mole of dissolved zinc will provide 2 moles of hydroxide for neutralization.

$$\begin{aligned}\text{Mmoles to first end point} &= \left(\text{cm}^3_{\text{HCl}} \right) (M_{\text{HCl}}) \\ &= \text{mmoles OH}^- + \text{mmoles CO}_3^{-2}\end{aligned}$$

$$\text{Additional mmoles to second end point} = (\text{additional cm}^3 \text{ HCl})(M_{\text{HCl}})$$

$$= \text{mmoles CO}_3^{-2} + \text{mmoles for KSCN blank}$$

For the procedure described above, 28 cm³ of saturated KSCN should be titrated to determine the blank (3 ml KSCN are contained in the aliquot and 25 ml more are added). If samples are diluted in a different manner, appropriate quantities should be taken. If the carbonate content is large and accuracy is needed of only a few percent, the blank can be neglected.

Since 1/5 aliquots are titrated,

$$[\text{OH}^-] \text{ in electrolyte} = \frac{5 \times \text{mmoles OH}^-}{\text{Sample volume}}$$

$$[\text{CO}_3^{-2}] \text{ in electrolyte} = \frac{5 \times \text{mmoles CO}_3^{-2}}{\text{Sample volume}}$$

If weighed samples are used,

$$\text{mg K}_2\text{CO}_3 = \text{mmoles CO}_3^{-2} \times 138.2$$

$$\text{wt \% K}_2\text{CO}_3 = \text{mg K}_2\text{CO}_3 \times 100/\text{mg sample}$$

$$\text{mg KOH} = \text{mmoles OH}^- \times 56.11$$

$$\text{wt \% KOH} = \text{mg KOH} \times 100/\text{mg sample}$$

If one wishes to express the results as ZnO + KOH + K₂CO₃, it is necessary to analyze a separate portion of electrolyte for zinc, probably by titration with EDTA. See appendix for further details. In this case,

$$\text{mmoles KOH} = \text{mmoles OH}^- - 2(\text{mmoles Zn})$$

CONCLUDING REMARKS

The data presented here show that battery electrolyte containing zinc can be analyzed conveniently and accurately for hydroxide and carbonate using a saturated solution of KSCN to complex the zinc at the first end point. Accuracy obtained is 3 to 4 parts per 1000. The titration then differs from the usual determination of hydroxide and carbonate in only two aspects. First, the first end point is shifted from 8.3 to 7.9 - 8.0, so that if an indicator is used to determine the end point, m-cresol purple or phenol red must be used instead of phenolphthalein. Secondly, a small but noticeable correction must be made for the amount of acid required to titrate the KSCN added between the two end points.

The simplification of the analysis for alkaline battery electrolyte enables identification of the modes of failure of these batteries to be determined more readily and is useful in research to lengthen the life of alkaline batteries.

APPENDIX

For the convenience of the reader a few details of our method of titration for zinc are included. An aliquot of the solution of battery electrolyte that has been diluted with KSCN as described above is added to 5 cm³ of pH 10 buffer (~8 M NH₃, 1.5 M NH₄NO₃). The aliquot should contain 0.05 or 0.10 cm³ of the original electrolyte. The solution is titrated with 0.005 M EDTA. The added KSCN does not interfere since the EDTA complex of zinc is stronger than the SCN⁻ complex. Colorimetric determination of the end point can be used (ref. 6), but if an automatic titrator is available, it is convenient to use amperometric titration with dual polarized amalgamated silver electrodes (refs. 7, 8, and 9). A potential difference of about 200 mV is maintained between the electrodes, and the titration is carried out until a sharp rise in the current is noted. Ammonium nitrate is used in the buffer rather than ammonium chloride to avoid interference of the chloride with the mercury electrode.

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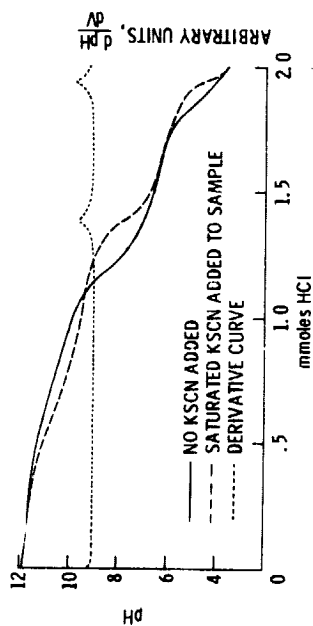


Figure 1. - Titration curves of simulated battery electrolyte equivalent to 5.27 M K_2CO_3 , 8.59 M KOH, and 1.27 M Zn^{+2} . Calculated meq (including 0.021 meq correction for KSCN blank at 2nd end point); 1st end point 1.386 \pm 0.003, 2nd end point 1.934 \pm 0.003. Meq found; 1st end point 1.386 \pm 0.004, 2nd end point 1.937 \pm 0.006.

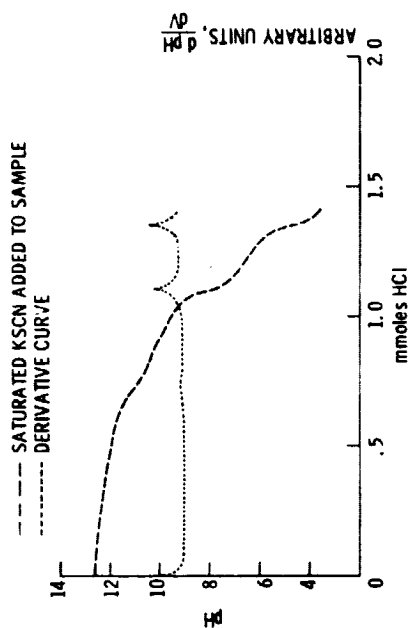


Figure 2. - Titration curves of simulated battery electrolyte equivalent to 2.28 M K_2CO_3 , 8.66 M KOH, and 0.637 M Zn^{+2} . Calculated meq (including 0.018 meq correction for KSCN blank at 2nd end point); 1st end point 1.094 \pm 0.004, 2nd end point 1.341 \pm 0.004. Meq found; 1st end point 1.099 \pm 0.003, 2nd end point 1.349 \pm 0.004.

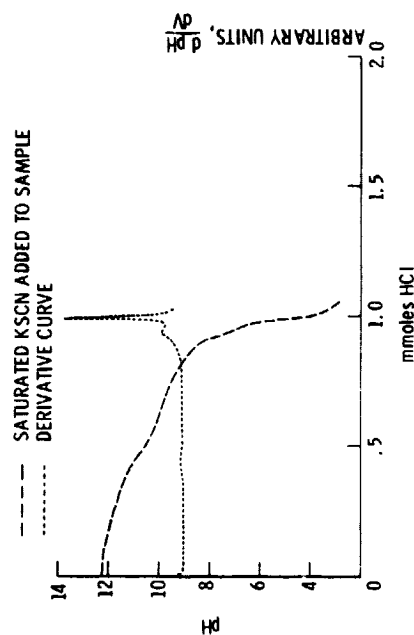


Figure 3. - Titration curves of simulated battery electrolyte equivalent to 0.46 M K_2CO_3 , 8.80 M KOH, 0.18 M Zn^{+2} . Calculated meq (including 0.018 meq correction for KSCN blank at 2nd end point); 1st end point 0.926, 2nd end point 0.990. Meq found; 1st end point 0.928, 2nd end point 0.987. (Insufficient data to give standard deviation.)